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Resistive switching characteristics and conduction mechanisms of nonvolatile memory devices based on Ga and Sn co-doped ZnO films

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ABSTRACT

Nonvolatile memory devices were fabricated utilizing Ga and Sn co-doped ZnO (GZTO) films formed by using a solution process method. X-ray diffraction patterns showed that the crystallinity of the annealed GZTO films was an amorphous phase. X-ray photoelectron spectroscopy spectra of the GZTO films depicted Zn – O, Ga – O, and Sn – O bonds. Current–voltage measurements on the Al/GZTO/indium-tin-oxide (ITO) devices at 300 K showed bipolar resistive switching behaviors. The resistances at both the low resistance state (LRS) and high resistance state (HRS) measured at 0.5 V for the devices maintain almost constant without any damage and breakdown above 130 s, indicative of the memory stability of the devices. A difference in the resistance between the HRS and the LRS was more than 1 order of the magnitude. The conduction mechanisms of the HRS in the set process for the Al/GZTO/ITO devices were dominated by a space-charge-limited current model.

1. Introduction

Resistive switching (RS) memory devices have been currently receiving considerable attention for promising applications in next-generation nonvolatile memory devices [1]. RS memory devices have become particularly interesting because of their low operating power, high density, and high switching speed. Recently, RS memory devices have been fabricated utilizing several types of metal-oxide semiconductors and other non-metal oxide compound semiconductors. The excellent bipolar switching characteristics, such as fast switching speed, long retention time, and high reliability, have been demonstrated in the ZnO-based resistive switching devices [2–4]. Among the various types of ZnO-based materials, transparent quaternary oxide thin films of InGaZnO, InZnSnO, and GaZnSnO (GZTO) have been extensively investigated because of their excellent physical properties of good uniformity, high mobility, and low cost [5–7]. Most of reported quaternary oxide systems have been formed by using chemical vapor deposition, RF magnetron sputtering, pulsed-laser deposition, and solution-processed methods [8–10]. Among the various deposition methods, a solution process has introduced to form oxide based materials due to its advantages, such as large area, low cost, high growth rate, and low temperature deposition [11–14]. Even though some investigations concerning the fabrication and electrical characteristics of the Ga and Sn co-doped ZnO film have been carried out [15], the investigations concerning the resistive switching characteristics and conduction mechanisms of the Ga and Sn co-doped ZnO film grown on the indium-tin-oxide (ITO)-coated glass substrates by using a solution process have not been conducted yet.

This paper presents data for resistive switching characteristics and conduction mechanisms of the Ga and Sn co-doped ZnO film grown on the ITO-coated glass substrates by using a solution process at room temperature. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the structural properties of the GZTO thin films, and current–voltage (I–V) measurements were carried out in order to investigate the resistive switching behaviors for the Al/solution-processed GZTO thin film/ITO device. The conduction mechanisms of the GZTO thin films were described by using theoretical modeling from the resistance slope of the I–V curves for the Al/solution-processed GZTO thin film/ITO devices.

2. Experimental details

A solution of the Ga and Sn co-doped ZnO precursor was synthesized by using a solution process and dissolving zinc acetate dehydrate [$(CH_3COO)_2Zn \cdot 2H_2O$], gallium nitrate hydrate [$Ga(NO_3)_3 \cdot H_2O$], and tin chloride pentahydrate [$SnCl_4 \cdot 5H_2O$], which were used as precursors for Zn, Ga, and Sn in 2-methoxyethanol at room temperature. A small amount of monoethanolamine (MEA) was introduced into the GZTO precursor solution to form a solution against any precipitate. The molar ratio of the 2-methoxyethanol:MEA was 10:1. The solution was stirred at 65 °C for 1 h to form a transparent and homogeneous substance, which was used as a coating solution after cooling to room temperature. The ITO-coated glass substrates were rinsed with ethanol and distilled water for several times and dried at room temperature. The precursor solution was filtered through a 0.20-μm polytetrafluoroethylene syringe filter and was spin-coated onto the ITO-coated glass substrate using a spin-

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coater at a speed of 3000 rpm for 30 s. A GZTO film was formed and baked at 130 °C for 30 min on a hot plate to evaporate the solvent and remove organic residuals. The spin-coating and baking procedures were repeated for several times. Then, the GZTO films were annealed for 1 h at 350 °C in air. A-200-nm-thick Al layer, acting as the top electrode, was deposited on the GZTO films for the electrical measurements by using a thermal evaporator equipment utilizing a metal shadow mask with a diameter of 200 μm. Subsequently, the resistive switching devices with an Al/GZTO/ITO/glass structure were fabricated to investigate memory effects. The electrical characteristics of the resistive switching devices were measured by using a semiconductor parameter analyzer (Keithley instrument 4200) at room temperature. The XRD measurement was performed by using a D/MZA-2500/PC (Rigaku) with Cu-Kα radiation ($\lambda = 0.15406$ nm). The XPS Theta probe (Thermo Fisher Scientific) was used to obtain the surface chemical composition of the films. The X-ray source gun was Al-Kα radiation with a beam diameter of 400 μm and an energy step size of 0.05 eV. The peaks were analyzed by using Avantage 5.91 analysis tool. Peak background average was 0.5 eV. The XPS data referenced at C 1 *s* at 284.5 eV.

3. Results and discussions

Fig. 1 shows the XRD pattern of the (a) solution-processed GZTO film/n-Si substrate and the (b) solution-processed GZTO film/ITO/glass substrate. Any XRD peak corresponding to the annealed GZTO thin films on the n-Si substrate or the ITO coated glass substrate is not observed, indicative of the amorphous phase of the GZTO thin film, as shown in Fig. 1(a) and (b). The amorphous nature of the GZTO film indicates that the deposition of the GZTO film is possible on various substrates, such as the flexible polyethylene terephthalate. The XRD peaks at 30°, 50°, and 60° are related to the ITO/glass substrate, as shown in Fig. 1(a) [16].

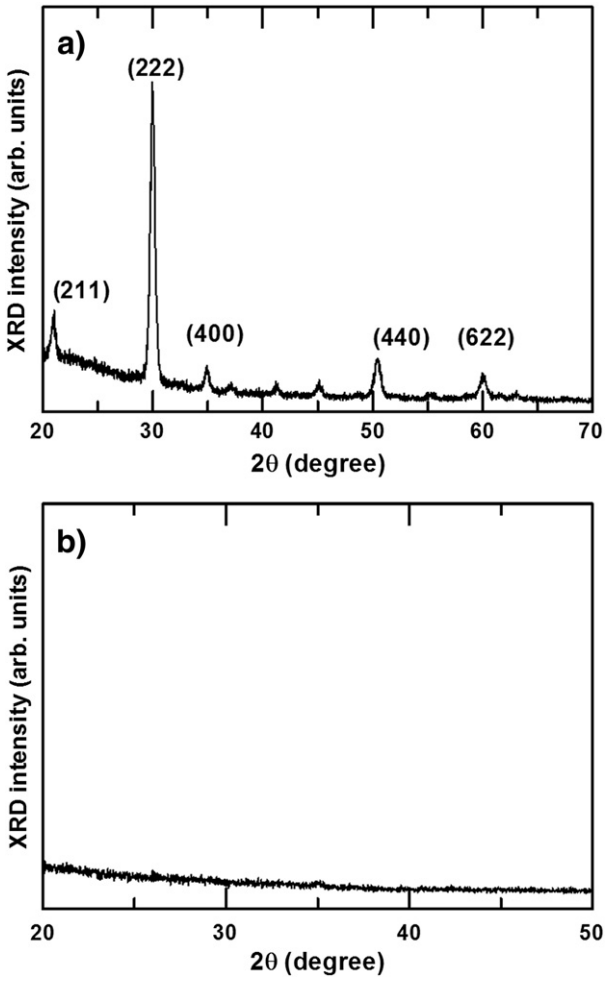

Fig. 1. X-ray diffraction patterns for the (a) GZTO films on the ITO-coated glass substrates and the (b) GZTO films on the Si substrates.

Fig. 2 shows Ga 2*p*, Zn 2*p*, Sn 3*d*, and O 1*s* of the XPS spectra for the GZTO films. The Ga $2p_{3/2}$ peak at 1117.6 eV, the Zn $2p_{3/2}$ peak at 1021.7 eV, and the Sn $3d_{5/2}$ peak at 486.2 eV correspond to the Ga – O, Zn – O, and Sn – O bonds, respectively [17]. The binding energy peaks of the Ga – O, Zn – O, and Sn – O bonds shifted to a higher energy in comparison with those of the Ga – Ga (1117.4 eV), Zn – Zn (1021.5 eV), and Sn – Sn bonds (484.6 eV) [18]. The XPS spectra for the O 1*s* peaks of the GZTO films are shown in Fig. 2(d). The binding energies of the O 1*s* peak for the GZTO film, as fitted by three Gaussian functions, are 532.7, 531.7, and 530.2 eV, as shown in Fig. 2(d). The higher binding energies at 532.7 eV for the GZTO films are attributed to the presence of loosely bound oxygens existing on the surface of the GZTO film and belonging to a specific specie of $-CO_3$, adsorbed H_2O, or adsorbed O_2 [19]. The lower binding energies of the O 1*s* spectrum at 530.2 eV are related to O^{2-} ions surrounded by Ga, Zn, and Sn atoms in the GZTO compound semiconductor [20]. The XPS intensity corresponds to the number of oxygen atoms in a fully oxidized stoichiometric surrounding region. The medium binding energies at 531.7 eV are associated with non-lattice oxygen (O^{2-}) ions, such as oxygen vacancies existing in oxygen-deficient regions within the GZTO film [21]. The presence of the significant numbers of O^{2-} ions in oxygen-deficient regions play an important role in the resistive switching behaviors, which allow to be operated without a forming process [22]. Non-lattice oxygen (O^{2-}) ions, such as oxygen vacancies existing in oxygen-deficient regions, act as the traps in the conduction mechanism of the HRS. Because Ga cations bind with oxygen and suppress the generation of oxygen defect sites, they play an important role for the carrier suppressor in the film. Therefore, the trap density in GZTO matrix can be controlled by various Ga concentrations.

The resistive switching behaviors and memory effects of the Al/GZTO/ITO device were investigated by using I–V curves. The bottom electrode was grounded while bias voltages were applied to the top electrode. Fig. 4 shows the I–V curves measured at the voltage steps with an increment of 0.1 V from 0 to −1, −1 to 0, 0 to 1.5, or 1.5 to 0 V for the Al/GZTO/ITO device. The current compliance with 0.01 A was applied in order to prevent from permanent damage. Bipolar resistive switching behaviors clearly appeared in the I–V curves, as shown in Fig. 3. I–V curve for the device under applied voltages between 0 and −1 V showed the high resistance state (HRS). The current of the device at an applied voltage of −1 V abruptly increased, which corresponded to a switching from the HRS to the low resistance state (LRS), defined as the set process. The reset process from the LRS to the HRS occurred at an applied voltage less than 1.5 V, and the resistive switching behavior was achieved. The set and reset processes of the Al/solution-process GZTO/ITO device were similar to those of the memory device based on the sputtered InGaZnO thin film.

Fig. 4 shows the data-retention characteristics of the HRS and the LRS as functions of the time at room temperature. The resistances at both the LRS and the HRS measured at 0.5 V maintain almost constant without any damage and breakdown, conforming the good stability of the nonvolatile nature of the Al/GZTO/ITO device. This result indicates that the retention characteristic of the Al/solution-process GZTO/ITO devices provides promising applications in the memory device.

The conducting mechanisms of the current in the Al/GZTO/ITO devices were investigated by analyzing the I–V characteristics in a double logarithmic scale, as plotted in Fig. 5. The current in the LRS region linearly depends on the voltage with a slope of 0.95, indicative of the Ohmic-like behavior. The conduction mechanisms of the HRS in the set process are more complicated than those of the LRS. The set process in the HRS consists of the Ohmic conduction ($I \propto V$) in a low voltage region and a quadratic term ($I \propto V^2$) in a high voltage region, followed by a rapid increase in current. This result indicates that the conduction